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<b>(21) International Application Number:</b> PCT/GB91/00780 <b>(22) International Filing Date:</b> 17 May 1991 (17.05.91) <b>(30) Priority data:</b> 9011250.9 19 May 1990 (19.05.90) GB 9102143.6 31 January 1991 (31.01.91) GB <b>(71) Applicant (for all designated States except US):</b> THE DOW CHEMICAL COMPANY [GB/GB]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (GB). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> BALL, Jeffrey, Maurice [GB/GB]; Independence House, Vale Road, Otterspool, Stockport SK6 3LE (GB).		<b>(74) Agent:</b> RAYNOR, John; W.H. Beck, Greener & Co., 7 Stone Buildings, Lincoln's Inn, London WC2A 3SZ (GB). <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** WATER-ABSORBENT RESIN PARTICLES FOR ABSORBENT STRUCTURES**(57) Abstract**

Water-absorbent resin particles comprising a carboxyl containing water-absorbent resin characterized in that the water-absorbent resin is rendered adhesive by the incorporation of a thermoplastic polymer with hydrophilic character. Optionally, a flow control additive is also employed. In another embodiment the invention comprises water-absorbent structures or articles which comprise a woven or nonwoven mass of fibers of a desired shape characterized in that adhesivized water-absorbent resin particles of the invention are bound to the fibers of the woven or nonwoven mass of fibers. The particles must be prepared by blending water-absorbent resin particles containing carboxyl moieties with a thermoplastic resin having hydrophilic character until the mixture no longer flows freely and, optionally, adding to the water-absorbent resin particles and thermoplastic polymer mixture a flow control additive and blending until the mixture flows freely.

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## WATER-ABSORBENT RESIN PARTICLES FOR ABSORBENT STRUCTURES

This invention relates to novel water-absorbent resin particles, a process for the preparation of such water-absorbent resin particles and to absorbent structures containing the water-absorbent resin particles. The invention further relates to water-absorbent resin compositions with improved aqueous fluid absorption properties, and water-absorbent structures containing these water-absorbent resin compositions.

It is known to form woven and non-woven structures of cellulosic fibers, natural cotton fibers, synthetic fibers or mixtures thereof for use in absorbing aqueous fluids. In one example, the fibers are formed into open-structured absorbent webs, and in another, the fibers are thermally bonded to form complex structures. The fibers used in such structures can quickly absorb aqueous fluids and distribute them over the whole absorbent structure by capillary forces. The structures, in the absence of water-absorbent resin particles, have limited absorption capacity, and are very bulky due to the large amount of material needed to provide acceptable absorption capacity. Further, the

absorbent structures do not retain fluid under pressure. A means for improving the absorbency characteristics is to incorporate in the absorbent structures water absorbent resin particles which imbibe fluid to form a swollen hydrogel material, as described for example in  
5 US Patent 4,610,678. This hydrogel serves to retain the absorbed fluid even under pressure and gives the absorbent structure a "dry feel" even when wetted. In order to reduce the bulk of absorbent structures  
10 containing water absorbent resin particles, large volumes of the absorbent structure material can be replaced with small volumes of absorbent resin particles. The absorbent resin particles must quickly absorb fluids and retain such fluids to prevent leakage.  
15 Water absorbent resin particles (also referred to as superabsorbent polymers) are primarily used in personal care products to absorb body fluids, for example baby diapers, adult incontinence products, feminine hygiene products, and the like.

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Water-absorbing resins well known in the art include, for example, the hydrolyzate of a starch-acrylonitrile graft polymer as disclosed in US Patent  
25 3,661,815; the neutralization product of a starch-acrylonitrile acid graft polymer as disclosed in US Patent 4,076,663; the saponification product of a vinyl acetate-acrylic ester copolymer as disclosed in Japanese  
30 Laid-Open Patent Publication No. 14689/1977; the hydrolyzate of an acrylonitrile copolymer and the hydrolyzate of an acrylamide copolymer as disclosed in Japanese Patent Publication 15959/1978; the crosslinked products of these hydrolyzates and a self-curable poly(sodium acrylate) obtained by inverse phase

suspension polymerization as disclosed in US Patent 4,093,776; and the crosslinked product of partially neutralized polyacrylic acid as disclosed in Japanese Laid-Open Patent Publication 84304/1980.

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The absorbent structures demonstrate limited ability to retain the water-absorbent resin particles which are randomly dispersed throughout the structure in the desired locations. This can cause loss of the water-absorbent resin particles during the manufacturing process of such structures, irritation of the subject during the end use, such as, baby's skin when the structure is used as a disposable diaper. It is difficult to distribute the water-absorbent resin particles evenly within the absorbent structure. Further, the water-absorbent resin particles can migrate within the structure, causing a loss in absorbent properties of the entire structure. Such water-absorbent resin particles can agglomerate or be too close to one another. Water-absorbent resin particles in the presence of aqueous fluids form gels. If the gel particles of resins particles are too close to one another gel blockage can occur and the ability of the closely associated water-absorbent resin particles to fully absorb aqueous fluids is significantly reduced. In order to maintain a minimum absorption capacity, more water absorbent resin particles may be used than would be necessary in the absence of the risk of improper distribution and gel blockage. Further, in the preparation of water-absorbent structures, handling and cutting can cause loss of water-absorbent resin particles from the structure resulting in waste, and could present industrial hygiene problems.

Water-absorbent structures function to remove aqueous fluids from a source and retain such aqueous fluids. The structures contain hydrophilic fibers which are designed to absorb and transport the aqueous fluid quickly to the interior structure by capillary and wicking means. Such fibers transport the fluid to the water absorbent resin particles which absorb and retain the aqueous fluids. One problem associated with such water-absorbent structures is the speed of absorption of fluids from the exterior of the structure by the fibers. EP 90,311,527.7 and GB-A-2237205 disclose a method of increasing the rate of aqueous fluid flow into the absorbent structures, such as a baby diaper or feminine hygiene napkin, by the addition of a surface active agent to the body side of the membrane of the absorbent structure. The surface active agent has the effect of reducing the surface tension of the body fluid or aqueous fluid to enhance the speed at which said aqueous fluid passes through the body side of the membrane of the absorbent structure and into the fiber structure. This method of reducing the surface tension of aqueous body fluids is extremely effective in achieving rapid flow and distribution of the body fluid throughout the absorbent structure. However, this reduction of surface tension has the disadvantage of impairing the ability of the absorbent fiber structure to hold and retain the aqueous body fluid. Water-absorbent resins are included within the structure to aid in retaining such fluids. A problem associated with the use of water-absorbent resin particles is that the speed of absorption of the hydrophilic fibers in the structure is faster than the speed of absorption of the water-absorbent resin particles. Therefore, there is a

time differential between absorption of the aqueous fluid by the hydrophilic fibers and absorption of the fluid by the water-absorbent resin particles. During this time differential, there is a risk that the absorbent structure could lose such aqueous fluid before being absorbed and bound by the water-absorbent resin structures.

What is needed is a water-absorbent resin particle which can be effectively distributed within a absorbent structure and a means of effectively retaining the water-absorbent resins at the desired points in the absorbent structure.

In one embodiment the invention provides water-absorbent resin particles comprising a carboxyl containing water-absorbent resin, wherein the water-absorbent resin particles also comprise a thermoplastic polymer with hydrophilic character. Optionally, the particles also comprise a flow control additive. In another embodiment the invention comprises a water-absorbent structure which comprise a woven or non-woven mass of fibers having bound thereto particles as described above.

In another embodiment, the invention provides a process for preparing water-absorbent resin particles having adhesive properties which comprises blending water-absorbent resin particles containing carboxyl moieties with a thermoplastic resin having hydrophilic character until the mixture no longer flows freely and, optionally, adding to the water-absorbent resin

particles and thermoplastic polymer mixture a flow control additive and blending until the mixture flows freely.

5           The flow control additive can comprise an inorganic material which functions to give the composition flowability without tackiness. Alternatively, the flow control additive can comprise a  
10 water-soluble polymer which functions to increase the viscosity of aqueous fluids and which further functions to restore the flowability of the mixture of water-absorbent resin and thermoplastic polymer. In the embodiment where the flow control additive is the water-  
15 soluble hydrophilic polymer, the absorbent resin composition improves the function of the water-absorbent structures into which they are incorporated as the flow control additive increases the viscosity of aqueous  
20 fluids absorbed by the structure such that the absorbent fluid cannot easily be released by the structure before being bound by the water-absorbent resin particles.

          The adhesivized water-absorbent resin particles  
25 of the invention can be more effectively distributed within absorbent structures, and facilitate the maintenance of such effective distribution. As a result the invention allows the preparation of absorbent  
30 structures where gel blockage is minimized. Further, the use of such adhesivized water-absorbent resins result in less loss of resin during manufacturing and handling of the water-absorbent structures and prevent the problems associated with such loss. The adhesivized water-absorbent resin particles of the invention allow more efficient use of such particles in water-absorbent



structures, and allow the fabricator to use the optimum amount without significant waste. In those embodiments where the flow control additive is a water-soluble hydrophilic polymer, the retention of fluids by the absorbent structure is significantly enhanced.

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Adhesivized as used herein refers to resin particles that are modified such that at a later time they can be adhered to a portion of an absorbent structure, e.g. to the fibers of an absorbent structure.

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The water-absorbent resins useful in this invention are well-known to those skilled in the art. In particular, water-absorbent polymers useful in this invention are water-absorbent polymers which contain carboxyl moieties. Among preferred carboxyl containing water absorbent polymers are hydrolyzates of starch-acrylonitrile graft copolymers, partially neutralized products of a starch-acrylic acid graft copolymers, saponification products of vinyl acetate acrylic ester copolymers, hydrolyzates of acrylonitrile copolymers, crosslinked products of hydrolyzates of acrylonitrile copolymers, hydrolyzates of acrylamide copolymers, crosslinked products of hydrolyzates of acrylamide copolymers, partially neutralized products of polyacrylic acids and crosslinked products of partially neutralized polyacrylic acids.

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Especially preferred are alkali metal acrylate-type polymers obtained by copolymerizing 100 parts of an acrylic acid-type monomer composed of 1 to 50 mole percent of acrylic acid and 50 to 99 mole percent of an

alkali metal acrylate and 0 to 5 parts by weight of a crosslinkable monomer in aqueous solution in a monomer concentration of at least 20 percent by weight. In another preferred embodiment the alkali metal acrylate-type polymers are obtained by polymerizing acrylic acid and post neutralizing the polymer with an alkali metal base.

There is no limitation to the amount of the carboxyl groups of the water-absorbing resin. Preferably, at least 0.01 equivalent of carboxyl groups are present per 100 g of the water-absorbing resin. In the case of the partially neutralized polyacrylic acid, the proportion of the unneutralized portion is preferably 1 to 50 mole percent. In one preferred embodiment the water-absorbent resins are crosslinked at or near the particle surface by a polyhydroxy compound capable of reacting with the carboxyl moieties of the water-absorbent resin and may optionally have coated on or bound to the surface a non-ionic surfactant with an HLB from 3 to 10.

The polyhydroxy compound which is used as a surface crosslinking agent is a compound which contains at least two hydroxyl groups which are capable or readily reacting with the carboxyl groups of the water-absorbent resin, and which is capable of being dispersed over the surface of a water-absorbent resin particle. Preferably, the polyhydroxy compound used in this invention comprises ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycols, glycerol, polyglycerol, propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycols,

diethanolamine, triethanolamine, propane diol, butane diol, hydroxy terminated oxyethylene-oxypropylene block copolymers, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, trimethylolpropane, pentaerythritol, sorbitol, mannitol, sugars, sugar derivatives or the like. More preferred polyhydroxy compounds include diethylene glycol, triethylene glycol, glycerol, propylene glycol, trimethylol propane, pentaerythritol or sorbitol. Even more preferred are sorbitol or glycerol.

The surfactants which may be coated on the surface of, or bound to the surface of the water-absorbent resin particles are nonionic surfactants having an HLB in the range of 3 to 10 and which are dispersible in water. Preferable surfactants comprise sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, glycerol or polyglycerol fatty acid esters, polyoxy ethylene alkyl ethers, polyoxyethylene alkylphenol ethers, polyoxyethylene acyl esters, sucrose fatty acid esters or modified surface active polyesters. More preferred surfactants are polyethoxylated sorbitol lanolin derivatives, for example a surfactant available from ICI under the Tradename G1425. A sufficient amount of surfactant is used to facilitate a homogeneous distribution of the surface crosslinking agent on the surface of the gel particles, to improve the processability of the gel by reducing its stickiness, to reduce the tendency of the dried powder to agglomerate when exposed to humid air or water, and to bind fine dust of the water-absorbent resin.

The water-absorbent resins are adhesivized by contacting and blending with a thermoplastic polymer with hydrophilic character. Thermoplastic as used herein refers to a polymer which softens, flows and becomes tacky at elevated temperatures. For the purposes of this invention, the polymer must soften, begin to flow and become tacky at a temperature which does not harm the water-absorbent resins or materials from which the water-absorbent structures are prepared and which does not cause the properties of the final water-absorbent resin structure to be significantly degraded. Preferably, the polymer begins to soften at a temperature at or above 35°C and more preferably at or above 70°C. As the absorbent resin structures could be and often are exposed to temperatures approaching 35°C, it is preferable that the thermoplastic polymer be relatively stable at temperatures approaching 35°C. Preferably the thermoplastic polymer begins to flow and become tacky at temperatures of 170°C or less, more preferably 130°C or less, and most preferably 80°C or less. The material used in the absorbent resin structure may be deleteriously effected by exposure to temperatures above 170°C.

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Hydrophilic character means herein that the thermoplastic polymer has a portion which demonstrates affinity for water. Such affinity for water can be indicated by its ability to dissolve or disperse in water. Thermoplastic polymers which have both a hydrophobic portion and a hydrophilic portion may be used in this invention provided they have the appropriate thermoplastic characteristics. Thus certain surfactants which have thermoplastic character may be

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used in the invention. Among preferred classes of thermoplastic polymers are the polyvinyl pyrrolidone polymers, copolymers of polyvinyl pyrrolidone and vinyl acetate, polyethylene oxides, and polyethoxylated surfactants having a hydrocarbon cap. Hydrocarbon cap  
5 means herein a hydrophobic hydrocarbon moiety at one end of the polyethylene oxide chain. Such hydrocarbon caps can be aromatic, aliphatic, or have both aromatic and elevatic components. In one preferred embodiment, the  
10 hydrocarbon cap is a nonyl-phenoxy moiety. Examples of surfactants which are useful as the thermoplastic polymer with hydrophilic character include Synperonic NP 35 available from ICI, straight chain fatty alcohol  
inititated ethrylates such as Lutensol AO 30 available  
15 from BASF, and ocyl phenoxy ethrylates Triton X-100 available from Rohm & Haas.

Among more preferred thermoplastic polymers  
20 useful in the invention are the polyvinylpyrrolidones, polyvinylpyrrolidone vinyl acetate copolymers, and the polyethylene oxide based materials. Most preferred thermoplastic polymers are the polyvinyl pyrrolidones.  
25 Polymers of a wide range of molecular weights may be used in the invention, provided the above-mentioned characteristics are exhibited by the polymers.

The optional flow control additive functions to  
30 maintain the flowability of the composition of the invention. There are two classes of flow control additives which can be used. One class comprises an inorganic material which functions to improve and maintain the flowability of the adhesivized water-  
absorbent resins particles of the invention. Such

materials are well-known to those skilled in the art. Examples of materials which may be used include zinc oxide, talc, silica powders and the like. The most preferred of this class of flow control additives is zinc oxide. In a second embodiment the flow control additive can be a polymer which dissolves in or is dispersible in aqueous based fluids and increases the viscosity of aqueous fluids in which it is dissolved or dispersed. Such polymers are well-known to those skilled in the art. Among preferred classes of such polymers are polymers derived from carbohydrates, and modified polymers derived from carbohydrates. Included are the polysaccharides, modified polysaccharides, xanthum gums, and guar gums. Preferred polysaccharides are the cellulosic materials such as alkyl substituted cellulose, hydroxyalkyl substituted cellulose and the like, examples of such are cellulose, methylcellulose, ethylcellulose, hydroxyethyl cellulose and hydroxypropyl cellulose. In another preferred embodiment a mixture of guar and Xanthum may be used as the hydrophilic polymer.

The inclusion of the water-soluble polymers as flow control additives results in absorbent resin composition which causes aqueous fluids in contact with such composition to have an increased viscosity. By increasing the viscosity of such aqueous fluids such aqueous fluids are retained for a significant period in the absorbent structure while the water-absorbent resins absorb the aqueous fluid and bind them within the structure.

The water-absorbent resin is contacted with a sufficient amount of thermoplastic polymer to adhesivize substantially all of the resin particles. If too much thermoplastic polymer is used, the ability of the water-absorbent resin to absorb aqueous fluids will be deleteriously effected. Conversely, if an insufficient amount of thermoplastic polymer is used, all of the water-absorbent resin particles will not be adhesivized. Preferably, at least one part of thermoplastic polymer per hundred parts of water-absorbent resin is used, more preferably at least 3 parts by weight of thermoplastic polymer per hundred parts by weight of water-absorbent resin. Preferably, 20 parts by weight or less of thermoplastic polymer per hundred parts of water-absorbent resin is used, more preferably 10 parts by weight or less and most preferably 8 parts by weight or less are used. It is believed that by choice of a polymer which has hydrophilic character, such polymer when contacted with the water-absorbent resins at ambient temperature forms a physical bond on the surface of the water-absorbent resin particle. As the thermoplastic polymer bound to the surface of the water-absorbent resin particle blocks access of aqueous fluids to the water-absorbent resin particle, if too much thermoplastic polymer is used, the ability of water to come in contact with the water-absorbent resin particle is significantly reduced.

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The amount of flow control additive which is used is dependent upon the class of flow control additive chosen. In that embodiment where the flow control additive is an inorganic inert material, an amount which results in free flow of the composition of

the invention is used. The effective lower limit is that minimum amount which results in free flow of the adhesivized water-absorbent resin composition of the invention. The upper limit is based on economics. In a preferred embodiment, at least 0.25 parts by weight per hundred parts of water-absorbent resin is used. In a more preferred embodiment at least 0.5 parts by weight of flow control additive per hundred parts of water-absorbent resin is used. Preferably, one part by weight or less of flow control additive is used per hundred parts of water-absorbent resin. In that embodiment where the flow control additive is a water-soluble polymer which increases the viscosity of aqueous fluids into which it is dissolved, a sufficient amount is added to allow the adhesivized water-absorbent resins to freely flow. If too little of such flow control additive is used, the adhesivized water-absorbent resins will not flow freely. If too much is used, the functioning of the water-absorbent resin structure may be deleteriously effected. In this embodiment, preferably, one or more parts by weight of such flow control additive per hundred parts of resin is used, more preferably 5 parts by weight and most preferably at least 10 parts by weight. Preferably 20 parts by weight per hundred parts of water-absorbent resin are used, more preferably 15 parts by weight or less are used, and most preferably 12 parts by weight or less are used.

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The adhesivized water-absorbent resin compositions of this invention may be prepared by the following process. The water-absorbent resin particles are contacted with a sufficient amount of thermoplastic polymer with a hydrophilic character and blended under



conditions such that the resin particles become adhesivized. More particularly, the thermoplastic polymer and water-absorbent resin particles are blended by standard means at ambient temperature until the composition is well mixed. Evidence that the composition is well-mixed is indicated by the material becoming fluffy and demonstrating poor flow characteristics. Temperatures other than ambient may be used as long as it does not deleteriously effect the properties of the adhesivized resins. The time period for such blending depends on the scale at which the blending occurs the type of mixer used and whether a batch or continuous process is used, and can be empirically determined as described before. In a continuous process at least 2 to 3 seconds contact time is preferred. In a batch process as little as five seconds contact time may be used and as much as 3 to 4 hours may be used. Once the flow characteristics of the adhesivized resin deteriorate, the flow control additive can optionally be added and blending may continue. This blending can continue for a sufficient time such that the adhesivized resins flows freely. This can take place at any temperature which does not deleteriously affect the properties of the adhesivized water-absorbent resin, and most conveniently takes place at ambient temperatures. This blending continues for a time such that the material flows freely.. The time period for such blending depends on the scale at which the blending occurs the type of mixer used and whether a batch or continuous process is used, and can be empirically determined as described before.

In a continuous process at least 2 to 3 seconds contact time is preferred. In a batch process as little as five seconds contact time may be used and as much as 3 to 4 hours may be used. Blending can occur by any means which

effectively results in contact of all of the components. Such means well-known to those skilled in the art, and the choice of such is not critical to the invention.

5           The adhesivized water-absorbent resins of the invention are primarily used by incorporating them into absorbent structures. Such structures are primarily composed of natural and/or synthetic fibers, the fibers can be formed into woven and non-woven structures. Such  
10 structures are well-known to those skilled in the art. The water-absorbent resins of this invention can be contacted with finished structures or mixed in with the component parts prior to formation of the structure. In  
15 general, the adhesivized absorbent resins of the invention are incorporated into the absorbent structure and the absorbent structure is exposed to temperatures at which the thermoplastic polymer softens and becomes tacky. Under such conditions, the adhesivized water-  
20 absorbent resin particles are then bound to fibers of the absorbent structure. The thermal bonding technique results in fixating the water-absorbent resin particles in the absorbent structure. This prevents loss of  
25 absorbent resin particles during handling and prevents migration and agglomeration of water-absorbent resin particles.

30           In one embodiment absorbent resin structures are prepared by what is known in the art as a lofting process. In such process a mixture of fibers is laid down, and the fibers are heated to expand the structure. In such process the fibers can either be pretreated with the adhesivized water-absorbent resin or if the temperature of the lofting process is high enough, the

adhesive structures can be bound to the fibers during the lofting step, provided the lofting temperature is sufficient to cause the thermoplastic polymer to soften and become tacky. In another embodiment, absorbent structures are prepared via a thermal bonding process.

5 In such process, a mixture of hydrophilic fibers and hydrophobic thermoplastic fibers are mixed and water-absorbent resin particles are contacted with such mixture. Thereafter the mixture of fibers and water-

10 absorbent resin particle is exposed to temperatures at which the thermoplastic polymer with hydrophilic character and the thermoplastic fibers of the structure begin to flow and become tacky such that the mass of fibers and resin become bound together upon cooling.

15 Synthetic fibers such as polyester, and polyolefin and natural or regenerated cellulosic fibers are preferably used. Preferably, the structure comprises a mixture of hydrophilic fibers, such as cellulosic and regenerated cellulose based fibers, with hydrophobic polyolefin and

20 polyester fibers. Preferably such mixture contains 20 percent or greater cellulosic fibers.

25 The particle size of the water-absorbent resin is not critical with respect to this invention. Particle sizes useful are those commonly known as useful in absorbent structures. In a preferred embodiment the particle size is less than about 2 millimeters, more

30 preferably 0.8 millimeters or less. Preferably the particles have a size of 0.2 millimeters or greater, and more preferably 0.5 millimeters or greater.

In one embodiment of the invention, water-absorbent resin particles of the invention can be

blended with the flow control additive which is a hydrophilic polymer soluble in water in the absence of the thermoplastic polymer. Such a composition can be used in those uses in which the adhesive is not required in the final structure. These compositions provide a means for improving the retention of aqueous fluids in an absorbent structure by holding the fluids in the structure while the absorbent resins are absorbing the liquid.

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EXAMPLES 1-6

Several thermoplastic polymers are contacted with water-absorbent resin particles and subjected to the following tests.

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Coating Affinity Test

Into a 500 ml glass jar are weighed 100 g of a water-absorbent resin particle. To this is added a portion of thermoplastic polymer. A top is placed on the jar and it is shaken for about 10 seconds. The physical condition of the mixture is noted after shaking. This is repeated for each thermoplastic polymer at levels of 5, 10, 15 and 20 g.

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Polymer Bonding

Mixtures of water-absorbent resin and thermoplastic polymer (5, 10, 15 and 20 parts of thermoplastic polymer per 100 parts of resin) are prepared by blending. The mixtures are separately sandwiched between two pieces of filter paper and heated on a ceramic hot plate. Evidence of thermal adhesion is noted at various temperatures.

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The water-absorbent resin particles are based on polyacrylic acid crosslinked with trimethylol propane and partially neutralized with sodium hydroxide to a level of 68 percent neutralization. The thermoplastic polymers are polyvinylidene pyrrolidone of three molecular weights (8000, 38,000 and 630,000); two polyethylene oxide based polymers (MW 100,000 and 600,000) and a low molecular weight polyvinyl alcohol,

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available from Air Products under the trade name Airvol 205.

#### Results Coating Affinity Test

5                    Good coating affinity is demonstrated by the polymer adhering to the water absorbent resin thermoplastic particles. Poor coating affinity is demonstrated by the presence of the thermoplastic  
10 polymer as a slowly settling dust once shaking is discontinued. The polyvinyl pyrrolidone demonstrated excellent coating affinity at all molecular weights. The polyethylene oxide polymers demonstrate limited affinity for the water absorbent resin by the presence of dust at  
15 10, 15 and 20 parts of thermoplastic polymer per hundred parts of resin. The polyvinyl alcohol exhibits excellent powder coating affinity, as only a slight amount of free dust is detected at 20 parts of polyvinyl alcohol.

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#### Results Bonding Test

                  The water absorbent resin blended with polyethylene oxide at 5 parts demonstrate good adhesion.  
25 Water absorbent resin particles coated with polyvinyl pyrrolidones of all three molecular weights demonstrate good bonding characteristics at 75°C. The polyvinyl alcohol coated water-absorbent resins demonstrate a slight adhesive character at 100°C. The results of both  
30 tests are compiled in Table I, L refers to low molecular weight, M refers to medium molecular weight, and H refers to high molecular weight.

Table I

Exam ples	Thermoplastic Polymer	Polymer Bonding	Coating Affinity
1	Polyvinyl pyrrolidone L	Good (75°C)	Excellent/all levels
2	Polyvinyl pyrrolidone M	Good (75°C)	Excellent/all levels
3	Polyvinyl pyrrolidone H	Good (75°C)	Excellent/all levels
4	Polyethylene oxide L	Good	Good / 5 parts; dust present at 10, 15 and 20 parts
5	Polyethylene oxide H	Good	Good / 5 parts; dust present at 10, 15 and 20 parts
6	Polyvinyl alcohol	Slight (100°C)	Excellent/ Slight dust at 20 parts

EXAMPLES 7-19

The properties of several adhesivized absorbent resin samples are determined. The following standard test methods are used.

25 Absorption Under Load

A nylon screen (37 diameter; 100 mesh) is put on top of perforated metal plate (holes with 5 mm) followed by a filter paper and finally by a stainless steel cylinder, whose both ends are open, of 26 mm inner diameter, 37 mm outer diameter and a height of 50 mm. 160 mg of water-absorbent resin particles are placed into the cylinder and evenly distributed, covered by a non-woven sheet of a diameter of 26 mm and finally pressed down with a teflon piston of 26 mm diameter

which carries the weight. The total weight of piston and cylinder is 104.4 g. The metal plate with the product in the cylinder on top is immersed into the 0.9 percent saline solution such, that the nylon screen and the water surface have the same level so that the filter paper and the water-absorbent resin particles are able to absorb water without any static pressure.

A soak time of one hour is applied. The plate is removed from the water reservoir and the excess water in the holes of the plate and in the nylon screen is soaked up by paper tissues. Then the weight is removed from the swollen gel and the gel is weighed. The weight ratio of saline solution absorbed under load to water-absorbent resin particles is the absorption under load (AUL).

#### Centrifuge Capacity

200 mg of water-absorbent resin particles are place within a sealable tea bag (63,5 x 76.2 mm), immersed for 30 minutes into a 0.9 percent saline solution and then centrifuged for three minutes at 1600 rpm. The weight ratio of saline solution absorbed to water-absorbent resin particles is the absorbency capacity (cc).

#### Speed of Absorption

A 6 cm diameter non-woven sheet available from Suominen Novelling T 391 is placed on the test plate of a Demand Absorbency Tester, available from Co-5MS, 0.50 g of water-absorbent resin is placed in the center 5 cm



of the non-woven sheet. A 0.9 percent NaCl in water solution is contacted with the resin. The time over which 10.1 ml of solution is absorbed by the resin is noted. This is the speed of absorption. The solution is added for 30 minutes. The absorbed volume is recorded.

5 20 filter papers (11.5 x 11.5 cm) are weighed. An 11.3 cm diameter non-woven sheet is placed over the swollen absorbent resin and 20 square filter papers 11.5 x 11.5 cm are placed over the non-woven sheet. Thereafter a load of 1917.7 g (11.5 x 11.5 cm) is placed over the

10 filter papers to give a load of 1973 g (3.85 kPa on 8 cm diameter area). After 5 minutes the load is released and the wetted filter papers are weighed. The maximum free absorption capacity (MFAC 91 g) is calculated as

15 follows:

$$\text{MFAC} = \frac{(V_1 - V_1^b) d}{0.5}$$

$V_1$  is the absorbed volume of the absorbent resin

20  $V_1^b$  is the absorbed volume of the filter papers and non-woven sheets of a blank, run without absorbent resin;

$d$  is the density of the saline solution (1.01)

25 The retention under pressure (PT, g/g) is calculated as follows:

$$R = \frac{V_1 \times d - (P_2 - P_1)}{0.5}$$

30  $P_1$  is the weight of the dry filter papers

$P_2$  is the weight of the wetted filter papers.

Bulk Density

Bulk density is calculated according to ASTM D-1895-69.

5 Flow Rate

Flow rate is determined according to ASTM D1895-69, and represents the time it takes 100 grams of material to flow out of a funnel having a 9.5 mm  
10 opening.

The water absorbent resin is a polyacrylic acid crosslinked with trimethylol propane and partially  
15 neutralized with sodium hydroxide, 68 percent. The water absorbent resin particles demonstrate two particle size distributions, Standard, 97 percent between 0.1 and 0.8 mm; and fine 99 percent less than 0.31 mm. The  
thermoplastic polymer used is polyvinyl pyrrolidone  
20 (PVP) of three different molecular weights; (L) 8000, (M) 38,000, and (H) 630,000. The results are compiled in Table II.

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Table II

Exa mp le	PVP MW	Particle Size	% by weight PVP	Centri- fuge Capacity g/g	PT g/g	Absorp- tion Speed min/sec	Demand Absor- bency ml/g	AUL g/g	Bulk Density g/ml	Flow Rate sec. per 100 g
7*	None	Std	-	29.1	31.1	1:37	48	25	0.60	10
8	L	Std	5	28.30	28.29	2:18	42.4	23.24	0.681	9.9
9	L	Fine	5	28.10	29.15	1:06	49.6		0.627	10.9
10	L	Std	10	27.75	27.20	2:47	40.2	21.08	0.704	9.8
11	L	Fine	10	27.10	25.95	1:12	42.4	20.81	0.637	10.8
12	M	Std	5	27.90	27.55	2:14	41.6	22.18	0.699	9.7
13	M	Fine	5	27.40	28.64	1:16	48.0	21.57	0.623	10.5
14	M	Std	10	26.36	27.58	2:14	40.9	20.12	0.695	9.7
15	M	Fine	10	27.00	28.26	1:12	47.4	20.82	0.628	10.9
16	H	Std	5	27.60	27.16	2:24	39.8	18.18	0.662	10.3
17	H	Fine	5	26.70	28.62	1:06	47.2	21.14	0.609	11.5
18	H	Std	10	25.20	27.03	2:54	40.2	18.40	0.652	11.4
19	H	Fine	10	24.80	26.38	1:15	43.6	16.56	0.602	13.0

Examples 20-22

83 parts by weight of the water absorbent resin described in the previous examples, 5 parts by weight of polyvinylpyrrolidone (8,000 mw) and 12 parts by weight of a hydrophilic polymer are put into a 200 ml plastic bottle. Two different hydrophilic polymers are separately used, methyl cellulose and a mixture of 12 percent xanthum and 88 percent guar. The bottle is closed and shaken for 2 hours. The compositions are then tested for centrifuge capacity, retention under pressure (PF), speed of absorption and Demand Absorption (DAT). A Control is prepared without the hydrophilic polymer using 95 parts absorbent resin and 5 parts polyvinylpyrrolidone. The results are compiled in Table III.

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Table III

Exa mp le	Hydrophilic Polymer	Centrifug e Capacity g/g	Retention under Pressure g/g	Demand Absorben cy (DAT) ml/g	Absorptio n Speed
20	-	31.1	31	40	1:37
21	Guar Xanthum	30.6	28.3	40	7
22	Methylcellulose	27.3	24.6	39	51

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Examples 23-24

A mixture of 130 grams of 56 percent by weight cellulosic fiber, 14 percent by weight synthetic fiber (polyethylene coated polypropylene fiber) and 30 percent by weight of a water absorbent resin comprising 95 percent of a partially neutralized polyacrylic acid crosslinked with trimethylol propane (68 percent with NaOH) and 0.5 percent by weight polyvinylpyrrolidone are

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contacted and thermally bonded at elevated temperatures such that a coherent matrix is formed.

A second sample comprises two substantially equal layers of non-woven cellulosic fibers with a layer of the water absorbent resin, without a thermoplastic polymer, disposed between the layers of cellulosic fibers. The sample comprises 90 percent by weight of the cellulosic fiber, and 10 percent by weight of water absorbent resin, and has a unit weight of 470 g/m<sup>2</sup>.

The two samples are tested as described hereinafter.

5 A Fritsch "Analysette 3" apparatus is arranged such that five sieves are arranged from top to bottom, 800 um, 400 um, 315 um, 200 um, and 100 um, with a pan below the screens. A sample of 5 to 10 grams is weighed. The sample is placed on the top sieve, and a cover is placed over the sieve. The sieve assembly is securely  
10 fastened in the Fritsch apparatus.

The apparatus is shaken for 15 minutes. The top screen with the sample is placed on a balance and the  
15 balance is set to 0.0. The sample is removed from the top screen and the screen is brushed. The empty screen is placed on the balance. The negative weight is the final weight of the sample on the screen. The weight  
20 loss of each sample due to shaking is calculated. The results are compiled in Table IV.

Table IV

Example	Beginning weight g	End weight g	% Weight Loss
23*	9.5	9.1	4
24	6.7	6.7	0

\* Not an example of the invention

The loss in Example 23 show loss of both water absorbent polymer and cellulosic fibers, it is difficult to determine the exact composition of the material removed from the absorbent structure.

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## PATENT CLAIMS:

1. Water-absorbent resin particles comprising a carboxyl containing water-absorbent resin characterized in that the particles also comprise a thermoplastic polymer having hydrophilic character.

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2. Water-absorbent resin particles according to Claim 1 wherein the thermoplastic polymer is present on surface of the water-absorbent resin particles.

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3. Water-absorbent resin particles according to Claim 1 or Claim 2 which is further characterized by the presence of a flow control additive.

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4. Water-absorbent resin particles according to Claim 3 which comprise from 1 to 30 parts by weight of thermoplastic polymer and from 1 to 15 parts by weight of flow control additive per hundred parts of carboxyl containing water-absorbent resin.

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5. Water-absorbent resin particles according to Claim 3 or Claim 4 wherein the flow control agent is an inert powder which promotes flow.

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6. Water-absorbent resin particles according to Claim 3 or Claim 4 characterized in that the flow control additive is a polymer which is soluble or dispersible in aqueous fluids and increases the viscosity of aqueous fluids.

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7. Water-absorbent resin particles according to any one of Claims 3 to 6 which comprises

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A) a carboxyl containing water-absorbent resin comprising a hydrolyzate of a starch-acrylonitrile graft copolymer, a partially neutralized product of a starch-acrylic acid graft copolymer, a saponification product of a vinyl acetate acrylic ester copolymer, a hydrolyzate of an acrylonitrile copolymer, a crosslinked product of a hydrolyzate of an acrylonitrile copolymer, a hydrolyzate of an acrylamide copolymer, a crosslinked product of a hydrolyzate of an acrylamide copolymer, a partially neutralized product of polyacrylic acid, or a crosslinked product of partially neutralized polyacrylic acid, wherein such water-absorbent resin may optionally be surface crosslinked by a polyhydroxy compound capable of reacting with the carboxyl moieties of the water-absorbent resin or may optionally have coated on the

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surface a nonionic surfactant having an HLB of from 3 to 10;

5 B) a thermoplastic polymer comprising a polyvinyl pyrrolidone, a polyvinyl pyrrolidone-vinyl acetate copolymer, a polyethylene oxide, or a polyethylene oxide capped on one end with a hydrophobic hydrocarbon moiety; and

10 C) a flow control agent comprising a polysaccharide, a modified polysaccharide or a mixture thereof.

15 8. A process for preparing water-absorbent resin particles according to any one of Claims 1 to 7 which process comprises

20 A) blending water-absorbent resin having adhesive properties containing carboxyl moieties with a thermoplastic resin having hydrophilic character until the mixture no longer flows freely; and

25 B) optionally, contacting the water-absorbent resin and thermoplastic polymer mixture with a flow control additive and blending until the mixture flows freely.

30 9. A water absorbent article comprising a woven or non-woven mass of fibers having bound thereto water-absorbent resin particles according to any one of Claims 1 to Claim 7.

10. A water-absorbent resin composition  
comprising water-absorbent resin particles containing  
carboxyl moieties characterized in that the composition  
5 also comprises a hydrophilic polymer which dissolves or  
disperses in aqueous fluids and which increases the  
viscosity of such aqueous fluids.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 91/00780

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl.5      C 08 J    3/12      C 08 L 101/02      A 61 L    15/58 A 61 L    15/60		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl.5	C 08 J                      A 61 L	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X, Y	EP-A-0 321 755 (CHEMISCHE FABRIK STOCKHAUSEN GmbH) 28 June 1989, see claims; page 2, lines 1-36; page 3, lines 12-14, 40-42; examples 7, 8	1-5, 8, 9
A	---	6, 7
Y	DE-A-2 222 780 (VEREINIGTE PAPIERWERKE SCHICKEDANZ & CO.) 22 November 1973, see claims 1-4; page 2, lines 5-14; page 4, line 15 page 8, line 17	1-5, 8, 9
X	GB-A-2 007 998 (UNILEVER LTD) 31 May 1979, see claims; page 2, lines 8-12; page 3, lines 1-7; examples 41-44	1, 2, 8, 9
A	GB-A-1 517 398 (AVTEX FIBERS INC.) 12 July 1978, see claims 1-14	1, 2, 9
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14-08-1991	17. 09. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px 10px; margin-right: 20px;">M. PEIS</div> <div style="font-family: cursive; font-size: 1.2em;">M. Peis</div> </div>	

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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9100780  
SA 47471

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82